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## THE ARSENIC CONTENT OF FILTER ALUM

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Specifications requiring arsenic free alum for water treatment by several European<sup>1</sup> purification plants suggested that it would be advisable to make determinations of the arsenic content of the filter alum used in this country and particularly of that used in the state of Illinois.

It is well known that products which are manufactured with the aid of commercial sulphuric acid quite generally contain more or less arsenic, depending upon the purity of the acid used. The poisonous character of arsenic compounds, even when present in small amounts, makes it of general interest and importance to have definite knowledge of the presence or absence of arsenic in any substance which enters directly or indirectly into foods or drinks. Sulphuric acid is used in the manufacture of filter alum and it is therefore quite essential, particularly to those who are in public health work, to know whether arsenic in any considerable amounts is being added to drinking water in the process of purification with alum.

We have been unable to find any definite published data relating to the arsenic content of filter alum. Dr. George A. Soper several years ago made an investigation of this problem, and referred to his results while discussing a paper by Mr. E. E. Wall<sup>2</sup> on "Water Purification at St. Louis, Missouri." Dr. Soper was discussing in par-

<sup>1</sup> Jour. f. Gasbel, 56, 882 (1913).

<sup>2</sup> Trans. Am. Soc. C. E., 60, 202-9.

ticular the use of sulphate of iron in water treatment and spoke in the following manner:

There is a final point which the speaker hesitates to mention, but, inasmuch as before this society it will probably be taken in the conservative spirit in which it is intended, and may lead to useful inquiries, it may be referred to briefly. It concerns the composition of the sulphate of iron used. . . . What are the impurities in this sulphate? How much arsenic is there in this sulphate? Some years ago the speaker had occasion to examine specimens of sulphate of aluminium from a good many filter plants and found arsenic in nearly all of them. It is true, that usually the arsenic was not present in large quantities, but it was easily discoverable, and in some of the samples it was present in sufficient amount to be of more than passing interest. The arsenic, of course, came from the sulphuric acid used in making the sulphate of aluminium, the sulphuric acid having been produced from pyrites which contained arsenic.

From Dr. Soper's first remark it is evident he realized that, due to the increasing public prejudice against the use of any material containing arsenic or other similar poison, a great injustice might be worked upon both the manufacturer and the plants that use alum for water treatment, by giving widespread publicity to this matter; at least, before all phases of the problem had been thoroughly investigated. The writers, too, are of this same opinion and so have refrained from mentioning the names of any manufacturers whose product have been examined and have also omitted the name of all filter plants outside the state of Illinois.

We have found but one other reference to the arsenic content of water treatment materials. In further discussion of the same paper and relative to sulphate of iron, Mr. E. E. Wall, in reply to Dr. Soper's statements, said:

The writer has a copy of a report . . . . in which it is stated that no arsenic was found in any of the samples tested and that the small quantity of arsenic in the sulphuric acid used in cleaning steel is, without doubt, removed in the cleaning tubs in the form of arseneuted hydrogen, thus leaving the liquors from which copperas is made, free from arsenic. Even if there should be a minute quantity of arsenic in the sulphate of iron, it is scarcely possible that this could remain in the water after treatment with the quantity of lime used at St. Louis.

The explanation of the absence of arsenic in sulphate of iron due to its loss as arsine is quite feasible but such is not the case with sulphate of aluminium. Filter alum is made by digesting bauxite with the required amount of sulphuric acid, consequently all or prac-

tically all of the arsenic present in the acid will remain in the finished product.

We have not been able to learn that anything has been done in this country to regulate the amount of arsenic in filter alum. The purification plants, at least in the state of Illinois, have made no effort to obtain an arsenic free article. The manufacturers of alum keep more or less accurate records of the arsenic content of their product. The writers have found only one producer who advertises "arsenic free alum." Neither the government nor any of the states has promulgated legislation regulating this product, although there is a regulation concerning arsenic in other substances entering into foods. The government has set a limit for arsenic in coal tar dyes and in baking powder of one part in 700,000. This very low limit, particularly when it is considered that only relatively small amounts of these substances are used in food preparation, shows that considerable importance is attached to the presence of arsenic and its compounds.

#### SAMPLES

In order that results might be of greatest value by showing the condition of the alums as they are actually used, as many samples as possible were first obtained directly from the water purification plants in Illinois. Twenty-six plants use alum in treating water. The purpose of the investigation was explained to the managers of each plant. They were asked to coöperate by furnishing a sample of the alum used, together with the name of the manufacturer or dealer supplying the same. Twenty-two of the plants very promptly complied with the request, and in nearly every case expressed decided interest in the subject with a wish to know the results of the investigation.

Owing to expense of transportation practically all of the alum used in Illinois is supplied by three manufacturers. In order to make our study more complete we have extended the scope of our investigations and have secured samples from practically all of the large manufacturers of alum in the country. In some cases the samples came directly from the producer, and in others from the water treatment plants. The specimens of alum were carefully sampled, ground and analyzed in duplicate by the following methods.

## METHODS OF ANALYSIS

The method used in obtaining most of the data given is a modified Gutzeit method, developed by Mr. Claude R. Smith<sup>3</sup> in his work on coal tar dyes and other food constituents. The results obtained by this method were in several cases checked by the Marsh-Berzelius method<sup>4</sup> and were found to agree. The Gutzeit method has been investigated by Sanger and Black<sup>5</sup> and others for quantitative work, and, when proper care is taken in the manipulation, has been found to give satisfactory results. The chief modification proposed by Smith is the use of paper sensitized with mercuric bromide instead of mercuric chloride, which had previously been generally used. The bromide gives more permanent stains and the standards can be kept longer. The method depends upon the formation of a dark orange stain when the generated arsine is brought in contact with the sensitized paper. The apparatus used is essentially as described by Smith. The generator is a 50 cc. wide mouth Erlenmeyer flask. This is connected with two upright tubes 8 cm. in length and 1 cm. in diameter, the lower containing lead acetate paper and the upper filled with cotton moistened with 5 per cent lead acetate solution. Fitted into the upper tube by means of a rubber stopper is a capillary tube 3 mm. in internal diameter and 12 cm. in length. This capillary is constricted at two joints about  $3\frac{1}{2}$  cm. from each end. By this means the sensitized paper is held in the center of the tube thus producing stains of equal length on both sides of the paper. Under uniform conditions, the length of the stain varies with the amount of arsenic present. A series of standard stains prepared from known amounts of arsenic are used for comparison. A convenient series is made from 2, 5, 7.5, 10 and 15 micromilligrams. The amount of arsenic in the weight of alum taken is determined by matching the stain it produces with the standards; it is then a matter of simple calculation to determine the percentage arsenic content or the parts per million of arsenic. A one gram sample will contain as many parts per million of arsenic as there are micromilligrams of stain obtained. For example, if one gram of alum produces a stain which matches the 5 micromilligram standard stain, then that alum contains 5 parts per million. One part per million

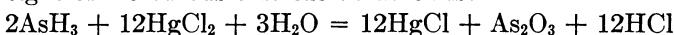
<sup>3</sup> U. S. Dept. Agr., Bur. of Chem., Circular No. 102.

<sup>4</sup> U. S. Dept. Agr., Bur. of Chem., Circular No. 99.

<sup>5</sup> J. Soc. Chem. Ind., 26, 1115 (1907).

is equivalent to 0.0001 of one per cent. A stain representing between 5 and 25 micromilligrams gives the most satisfactory results. A stain between these limits can be obtained by varying the weight of alum used.

For the analysis of alum containing more than 30 parts per million  $\text{As}_2\text{O}_3$ , another method proposed by Smith, was used. The generated arsine is passed into mercuric chloride solution (10 cc. of 5 per cent  $\text{HgCl}_2$  diluted to 100 cc.). According to Smith probably several different arsenides of mercury and some free arsenic are formed. These are oxidized by the excess of mercuric chloride, slowly in the cold and rapidly on heating, forming arsenous acid and mercurous chloride. The mercurous chloride can be filtered off and weighed and the arsenous acid in the filtrate determined by titration with iodine. In this way checks are obtained in the one determination. The equation used for the calculation of arsenic from the weight of mercurous chloride obtained is:



Thus  $1\text{As}_2\text{O}_3$  is equivalent to  $12\text{HgCl}$ .

As an alternative the conglomerate precipitate can be titrated by means of iodine. Sufficient potassium iodide is added to form the soluble double potassium mercuric iodide and then an excess of standard iodine solution. When all the precipitate has gone into solution the excess iodine is titrated with standard thiosulphate. The iodine absorption represents the oxidation of arsine to arsenic acid in which  $1\text{As}$  is equivalent to  $8\text{I}$ .

As usual all reagents used were tested to prove their freedom from arsenic.

#### DETERMINATION OF ARSENIC

Five grams of finely ground alum are dissolved in the generating flask in 30 cc. sulphuric acid (1-4) with the aid of heat. Four or five drops of a 40 per cent solution of stannous chloride in concentrated hydrochloric acid are added and the solution cooled. Four or five grams of arsenic free moss zinc are now added and the lead acetate tubes and capillary containing the sensitized strip are connected. The evolution of gas is allowed to proceed for at least one hour. The stain, after drying, is then compared with the standards. A steady, brisk but not violent evolution of gas should be maintained. This can be regulated by varying the acidity, volume of solution, amount of zinc and temperature. After a little experience very

uniform results can be obtained. In the determination of larger amounts of arsenic it is necessary to allow the evolution of gas to proceed for two or three hours.

The sensitized paper is made from heavy, close-textured drafting paper, cut into strips 2.5 mm. by 12 cm. These strips are soaked for an hour in a 5 per cent alcoholic solution of mercuric bromide. The excess solution is squeezed off and the strips allowed to dry.

The results from the samples obtained from the Illinois purification plants are given in Table I, those from outside the state in

TABLE I  
*Arsenic as As<sub>2</sub>O<sub>3</sub> in Filter Alums used in Illinois*

CITY	ARSENIC AS As <sub>2</sub> O <sub>3</sub>		GALLONS*
	Pts. per mil.	Per cent	
Cairo.....	1.6	0.00016	3213
Carlinville.....	1.8	0.00018	2856
Charleston.....	1.2	0.00012	4283
Chicago and Rogers Park.....	1.4	0.00014	3671
E. St. Louis and Granite City.....	0.8	0.00008	6425
Decatur.....	1.4	0.00014	3671
Elgin.....	1.6	0.00016	3213
Evanston.....	1.4	0.00014	3671
Ft. Sheridan.....	1.2	0.00012	4283
Hamilton.....	1.4	0.00014	3671
Kankakee.....	0.8	0.00008	6425
Kenilworth.....	1.4	0.00014	3671
Lawrenceville.....	3.0	0.00030	1713
Macomb.....	1.6	0.00016	3213
Moline.....	1.0	0.00010	5140
Mt. Carmel.....	2.0	0.00020	2570
Mt. Vernon.....	1.2	0.00012	4283
Pana.....	1.2	0.00012	4283
Quincy**.....	1.0	0.00010	5140
Quincy**.....	4.0	0.00040	1285
Rock Island.....	2.0	0.00020	2570
Rock Island Arsenal**.....	1.6	0.00016	3213
Rock Island Arsenal**.....	1.0	0.00010	5140
Streator.....	3.4	0.00034	1512

\* Gallons of water containing a minimum medicinal dose of 2 mgm. when the water is treated with 6 grains of alum per gallon, provided that all the arsenic remains in solution.

\*\* Two samples from different manufacturers.

Table II. In all cases the arsenic is recorded as arsenic trioxide,  $As_2O_3$ . Twenty-four samples from Illinois plants and seventeen from sources outside the state were analyzed.

The results obtained by analyzing alum used in Illinois clearly show that arsenic in exceedingly small amounts is always present in filter alums. We find a minimum of 0.8 part per million (0.00008 per cent) and a maximum of 4.0 parts per million (0.0004 per cent) of arsenic as  $As_2O_3$  in the alum used by Illinois water purification plants. If a water were treated with alum containing the maximum amount of arsenic found, at a rate of 6 grains of alum per gallon, an amount which is very seldom exceeded, and if all the arsenic were soluble and remained in the filtered water, since arsenic is not a cumulative poison, a person must drink 1285 gallons of the treated water at one time to obtain a medicinal dose of 2 mgms. From this it is readily seen that the arsenic content of filter alum used in Illinois is of no significance.

TABLE II  
*Arsenic in Filter Alum Obtained from Sources Outside the State of Illinois*

SAMPLE NO.	ARSENIC AS $As_2O_3$		GALLON*
	Pts. per mil.	Per cent	
1	0.5	0.00005	10280.0
2	1.2	0.00012	4283.0
3	1.2	0.00012	4283.0
4	1.4	0.00014	3671.0
5	2.6	0.00026	1977.0
6	2.6	0.00026	1977.0
7	4.0	0.0004	1285.0
8	4.0	0.0004	1285.0
9	5.0	0.0005	1028.0
10	20.0	0.0020	257.0
11	27.0	0.0027	190.0
12	31.0	0.0031	166.0
13	49.0	0.0049	105.0
14	280.0	0.0280	18.0
15	941.0	0.0941	5.5
16**	1240.0	0.124	4.0
17	1240.0	0.124	4.0

\* Gallons of water containing a minimum medicinal dose of 2 mgm. when the water is treated with 6 grains of alum per gallon, provided that all the arsenic remains in solution.

\*\* Nos. 16 and 17 were obtained from the same plant and are probably from the same lot of alum.

The samples obtained from sources outside the state showed a wider range in arsenic content. In one case there was 0.5 part per million (0.00005 per cent), and in nine cases there was more than in the highest Illinois sample, the maximum being 1240 parts per million of arsenic as  $\text{As}_2\text{O}_3$  (0.124 per cent).

If a water were treated with alum containing 1240 parts per million  $\text{As}_2\text{O}_3$ , at the rate of 6 grains per gallon and provided all the arsenic remained in solution, 0.13 part per million of arsenic as  $\text{As}_2\text{O}_3$  would be added and a medicinal dose of 2 mgm. would be contained in four gallons. This would be quite an appreciable amount and is more than should be added in water purification. However, owing to the insolubility of the arsenites and arsenates of calcium, magnesium, aluminium and iron, a large part of the arsenic would be removed with the precipitated aluminium hydrate. To determine the extent of this removal, if any, several experiments were carried out.

Two liters of water were treated at the rate of 6 grains per gallon with an alum containing 941 parts per million of  $\text{As}_2\text{O}_3$ . By this treatment 188 micromilligrams of  $\text{As}_2\text{O}_3$  were added. Forty micromilligrams of  $\text{As}_2\text{O}_3$  were recovered from the filtered water and 144 from the sludge. Thus only 22 per cent of the arsenic remained in solution.

Some water was treated at the rate of 20 grains per gallon with an alum containing 1240 parts per million of  $\text{As}_2\text{O}_3$ . Only 12 per cent remained in solution.

A sample of filtered water was obtained from the filtration plant using this latter alum. It had been treated at the rate of 200 pounds of alum per million gallons or at the rate of 1.4 grains per gallon. From this water only 7 per cent of the arsenic originally added was recovered from the solution. Thus a removal of 93 per cent of the arsenic was effected by the purification process.

#### CONCLUSION

Filter alum used by water purification plants in Illinois does not contain a significant amount of arsenic. Some filter alum used elsewhere contains a much larger amount of arsenic, but since at least 75 per cent of the arsenic added in the treatment of water with alum is removed with the precipitated aluminium hydrate, there is a strong probability that in no case a sufficient quantity of arsenic would be added to the filtered water to have therapeutic

significance. However, since alum containing an insignificant amount of  $As_2O_3$  can be readily obtained, the manufacturers should make an effort to keep the arsenic content of their product at a minimum and water works officials should demand an article practically free from arsenic.

We wish to express our appreciation of the assistance rendered by the manufacturers and water works officials who furnished us samples for examination.

#### DISCUSSION

MR. JAMES M. CAIRD: This was a very interesting paper which has just been presented by Dr. Bartow, and the large amount of data is of great value. The speaker does not like the use of the word alum, when really sulphate of alumina is meant. The general public has an awful horror of that word *alum*. Bringing up the subject of arsenic; the medical profession is very strict about the use of any water supply where alum or sulphate of alumina is used for purification, and now to think that Dr. Bartow is using alumina which contains arsenic: why, they are likely to go up in the air a little farther. Within two months a letter was received from an official of a state department of health, in which he says he would never be convinced that there was not some sulphate of alumina in the filtered water, although tests failed to show it. Now if that is the feeling in some of the health departments, if they think that there is arsenic too, what will they do about it?

The question of contaminating drinking water by using, for its purification, sulphate of alumina containing arsenic has often been discussed, and it has invariably been found that, even if the sulphate of alumina used contained determinable quantities of arsenic, no trace of arsenic was found in the filtered water. First, because part or all of the arsenic is precipitated with the ferric or alumina hydroxide formed in the purification process and filtered off. Second, because the small amount of sulphate of alumina used per gallon of water would bring down the arsenic content in the water to indeterminable traces, even if no arsenic was removed by the purification process. The Pharmacopeia of the United States requires that a chemical to be pure may contain not over ten parts per million of  $As_2O_3$ .

It is permissible to refer to the Royal British Committee appointed to investigate the so-called "Manchester beer scare" in 1901. This

committee gave the result of their investigations at the meeting of the London session of the Society of Chemical Industry in January, 1902. Their recommendation was chiefly on the method of testing for minute quantities of arsenic, and the discussion following was more or less of a farce. One member of the committee, a medical man, Dr. James Edmunds, doubted whether they had reached the real cause of the illness and death in the Manchester epidemic. He had been in the habit of prescribing arsenic and giving two or three milligrams per dose three times a day for a good many weeks, and had never known a case of arsenical neuritis to result. Most of the cases were proved to be alcoholic neuritis, not arsenical neuritis. One of the patients, who was confined to bed for three months with what was supposed to be arsenical neuritis, had been a total abstainer all his life, so that beer could hardly be blamed for his case. In short it has never been positively proven that the arsenic found in Manchester beer was the cause of the epidemic of neuritis in Manchester. Presumably that is why it is known as the "Manchester beer scare."

Arsenic is found so frequently everywhere in nature that it is impossible that natural water should not contain more arsenic than would ever be put in by using sulphate of alumina for its purification. All clays, ochres, iron ores, etc., contain arsenic, and all the waters from the most famous mineral springs, where people go for their health, contain arsenic in considerable quantities. Vichy, two parts per million; Carlsbad, varying from determinable traces to twenty-five parts per million. The late Sir Edward Franklin positively found arsenic in the atmosphere of London. Arsenic is found in the waters of the Rhine, Nile and in the Delaware river; in many vegetables, such as lettuce, beets, etc., but this must be considered dangerous ground, as all the acid phosphates used as manure contain large quantities of arsenic.

MR. CHARLES A. JENNINGS: The speaker had a practical application of this paper by Dr. Bartow, just a very short time ago. One of the packing firms in Chicago had a shipment of alum turned down by the government because it contained 125 p.p.m. of  $As_2O_3$ . As a result they were willing to sell that alum for about 15 cents per hundred pounds less than the regular price we were paying for alum.

MR. JAMES M. CAIRD: A case in the speaker's own family might be of interest; in this instance "arsenora" a compound of arsenic and gold has been used for the past fifteen years. The dose reaches, at times, as high as sixty drops per day before producing any trouble to the eyes.

DR. EDWARD BARTOW: We did analyze the water that had been treated with the alum containing arsenic, and actually found about nine per cent of the arsenic remaining in the filtered water. That was an actual test that we made.

MR. JAMES M. CAIRD: Did you try the raw water too, and could not find any there?

DR. EDWARD BARTOW: There was no arsenic in the raw water.

MR. A. ELLIOTT KIMBERLEY: Are there any cases on record suggesting arsenical poison through water?

DR. EDWARD BARTOW: Not to the author's knowledge.

MR. PHILIP BURGESS: Is there any germicidal action of the arsenic?

MR. WILSON MONFORT: Regarding that, the speaker has been watching with a good deal of interest the development of a mold in a tenth normal alkaline arsenious acid solution for some time, so arsenic is not necessarily fatal to vegetable organisms.